

Sixth Quarterly Report

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Project Title: Effect of Concentration and Temperature of Ethanol in Fuel Blends on Microbial and Stress Corrosion Cracking of High-Strength Steels

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For quarterly period ending: *December 14, 2009*

Technical Status

Technical efforts for this quarter have included field sampling from ethanol infrastructure, microbiological analysis of field samples, preparation of cyclic loading equipment, mechanical properties characterization, development of Bend and Fatigue Crack Growth Rate (FCGR) Testing, and development of a paper and presentation for presentation at an international conference.

Field Assessment and Microbiological Characterization

FGE containment tanks that capture ethanol spillage resulting from normal operation at fueling terminals have experienced corrosion problems. In some cases the tanks have been reported to smell like vinegar (acetic acid). As microbes are known to produce acetic acid while using ethanol as a substrate, they may be active in the ethanol contact water tanks. Corroded pipe steel associated with an ethanol contact water tank as well as tank bottoms from an ethanol contact water tank (Figure 1) have been acquired from a fueling terminal. Microscopy indicated the presence of microbes in the tank bottoms sample and further analyses, including 16S rRNA gene sequencing and cultivation experiments, are underway to determine what types of microbes are present in the sample.

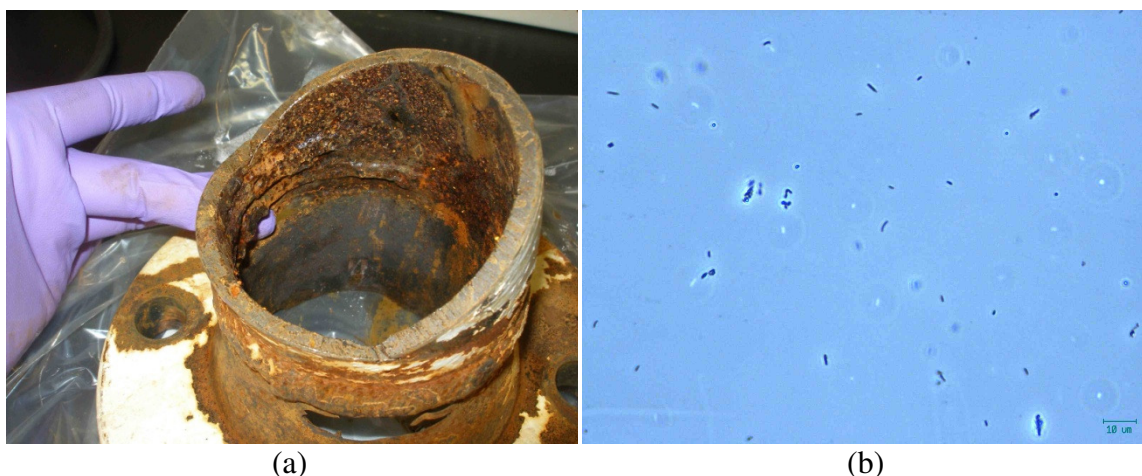


FIGURE 1: (a) Image of corroded pipe from an ethanol contact water system. (b) Light micrograph of ethanol contact water tank bottoms sample indicating the presence of microbes.

Laboratory cultivation efforts

Attempts to cultivate microbes from FGE environments have continued. Cultivation experiments have included the isolation of putative sulfate-reducing, spore-forming microbes from soils exposed to E10 (10% ethanol, 90% gasoline), E85 (85% ethanol, 15% gasoline) and E100 (fuel ethanol). Microbes have also been isolated from FGE infrastructure, and further characterization of these microbes is underway.

Attempts to cultivate microbes on steel coupons placed in the aqueous layer that forms under gasoline upon water addition has continued as shown in Figure 2. These experiments are designed to determine if microbes can survive in high-gasoline, low-water environments and if these microbes affect corrosion. Initial evidence suggests that microbes are present in environments with higher water concentrations, and current experiments are underway to determine if microbial activity/corrosion is present in systems with lower water concentration (1% water, 99 % gasoline).

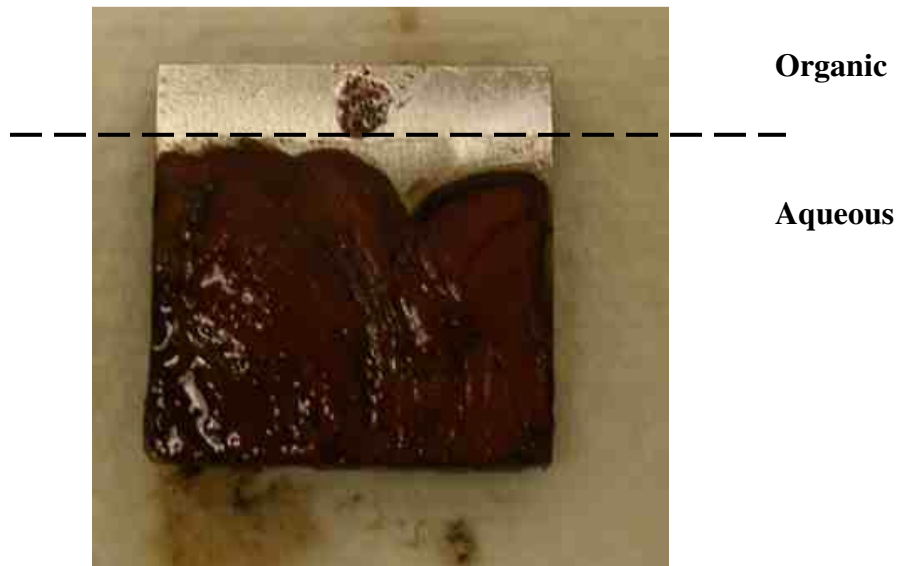


FIGURE 2: ASTM A36 steel coupon after exposure to a mixture of 1 pct water and 99 pct E10 fuel. The highly corroded portion of the coupon with visible slime was in the aqueous layer that forms under the organic (gasoline) layer. The less corroded portion of the coupon remained in the gasoline layer.

Bacillus species spores and manganese oxidation

Spores are a highly protective mode of life that some species of bacteria employ to survive harsh conditions. The spores of some *Bacillus* sp. have the ability to promote the oxidation of manganese. *Bacillus subtilis* SG-1 is a well-characterized, spore-forming microbe that produces manganese-oxidizing spores, and experiments have begun to determine if *B. subtilis* SG-1 spores can cause corrosion. These experiments have included exposing metal-coated glass slides to solutions containing metal-oxidizing spores. Further development and refinement of these experiments is necessary to determine if the spores enhance corrosion.

Mechanical Properties Characterization

The mechanical properties of the plate (A36) and two pipeline (X42 and X70) materials were characterized through tensile testing in accordance with ASTM E-8 in the longitudinal and transverse directions of the pipe. Tensile specimens were mechanically sectioned from the pipe and plate with the 12.7 mm (0.5 inch) of material nearest a flame cut edge removed to avoid testing the heat affected material from the flame cutting process. From the pipe material, tensile specimens in the longitudinal direction were sectioned and surface ground to a thickness of 3.43 mm (0.135 inch), and transverse tensile specimens were sectioned and ground flat to a thickness of 3.81 mm (0.150 inch) to achieve a flat specimen without the addition of plastic deformation through mechanical flattening. The longitudinal and transverse tensile specimens for the A36 plate material were surface ground to a thickness of 5.08 mm (0.200 inch). Figure 1 shows a picture of a tensile specimen in the transverse direction. Due to the curvature of the pipe, the X42 and X70 material transverse tensile specimens had some reduced thickness regions at the ends of the grip section. These reduced sections were away from the test area and sufficient flat grip area remained to meet testing requirements. Figure 3 shows a schematic drawing of the tensile specimen.

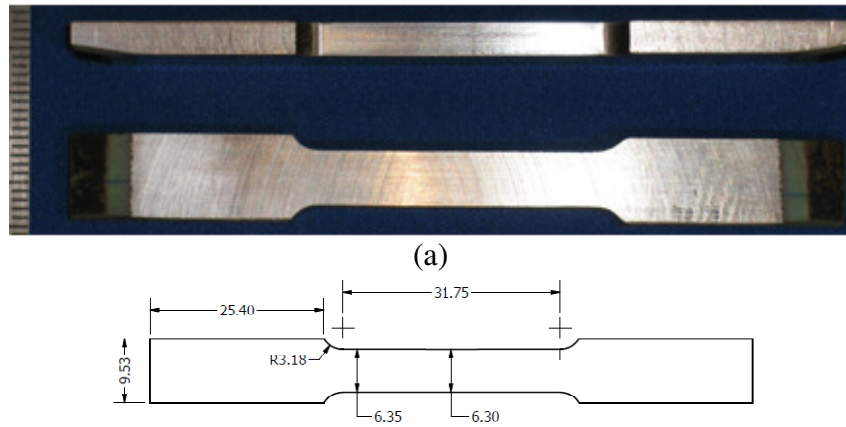


FIGURE 3: (a) Photograph of an ASTM E8 Sub-size tensile specimen for the X70 material in the transverse direction. The scale on the left is in millimeters. The reduction in grip area on both grip sections is from the curvature of the pipe section. (b) Schematic of tensile specimen geometry, units in mm, based upon ASTM E8-04 Figure 1 for the 6.35 mm (1/4 inch) wide specimen.

Uni-axial tensile tests were performed at room temperature on a servo-hydraulic load frame located at NIST in Boulder, CO. The tests were performed in displacement control using two constant displacement rates that correspond to two constant engineering strain rates. The rate at the start of the test was maintained low to satisfy ASTM E8-04 sub-section 7.6.3.2. The first and second displacement rates are $0.05 \text{ mm} \times \text{min}^{-1}$ and $0.5 \text{ mm} \times \text{min}^{-1}$ respectively, these displacement rates correspond to initial engineering strain rates of $2.67 \times 10^{-5} \text{ s}^{-1}$ and $2.67 \times 10^{-4} \text{ s}^{-1}$ respectively. The rate was increased after the specimen yielded to decrease the test time. The displacement rate was increased after approximately $\epsilon=0.02$ for each test. Strain was measured using a 25.4 mm (1 inch) 100% elongation extensometer. For each material and specimen orientation, triplicate tests were performed. From the tensile data, the 0.2% offset yield stress, ultimate tensile stress (UTS), and total elongation to failure (in a 25.4 mm gauge length) data were determined; these data are listed in Table 1.

TABLE 1 – Mechanical property data for the A36, X42, and X70 materials from tensile test data.

Specimen Material Type	Elastic Modulus (GPa)		0.2% Offset Yield Strength (MPa)		Ultimate Tensile Strength (MPa)		Total Elongation (%)	
	Average	STDEV	Average	STDEV	Average	STDEV	Average	STDEV
MIC A36L	175	3.3	292	3.1	451	0.5	37.8	1.8
MIC A36T	186	22.5	289	2.2	453	1.6	34.8	1.6
MIC X42L	190	5.9	397	4.2	491	1.0	30.9	0.3
MIC X42T	213	6.1	402	10.8	504	1.7	30.4	1.1
MIC X70L	215	8.8	561	14.5	655	9.1	24.9	1.2
MIC X70T	226	4.5	575	6.3	665	5.7	24.6	0.8

Engineering stress versus engineering strain data are plotted in Figure 4 for the A36, X42, and X70 materials in the longitudinal (open symbols) and transverse (closed symbols) directions. From these data, along with that in Table 1, demonstrate that the A36 material exhibit the best agreement between the longitudinal and transverse mechanical properties while the X70 exhibit the least agreement between the two test orientations. The specified minimum yield strength (SMYS) values for the A36, X42, and X70 materials are 248.2 MPa (36 ksi), 289.6 MPa (42 ksi), and 482.6 MPa (70 ksi) respectively. Comparison between the SMYS values for the 3 materials and their measured 0.2% strain offset yield strength values listed in Table 1 indicate that the three materials exceed their

SMYS requirements by a substantial margin, 43.8 MPa (6.3 ksi) for the A36, 107.4 MPa (15.6 ksi) for the X42, and 78.4 MPa (11.4 ksi) for the X70 grade.

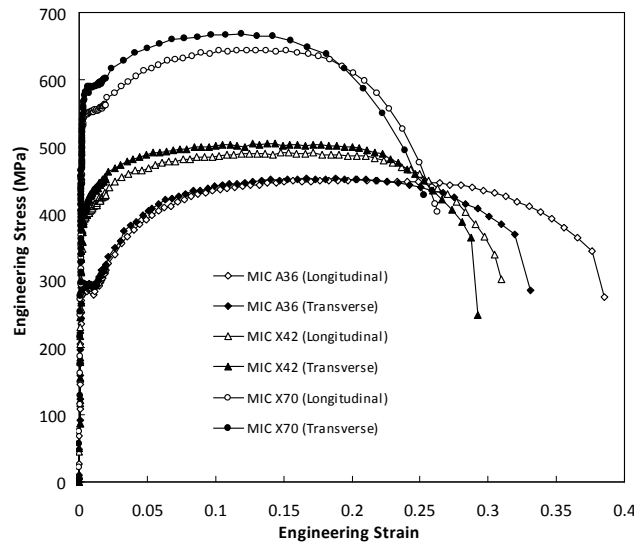
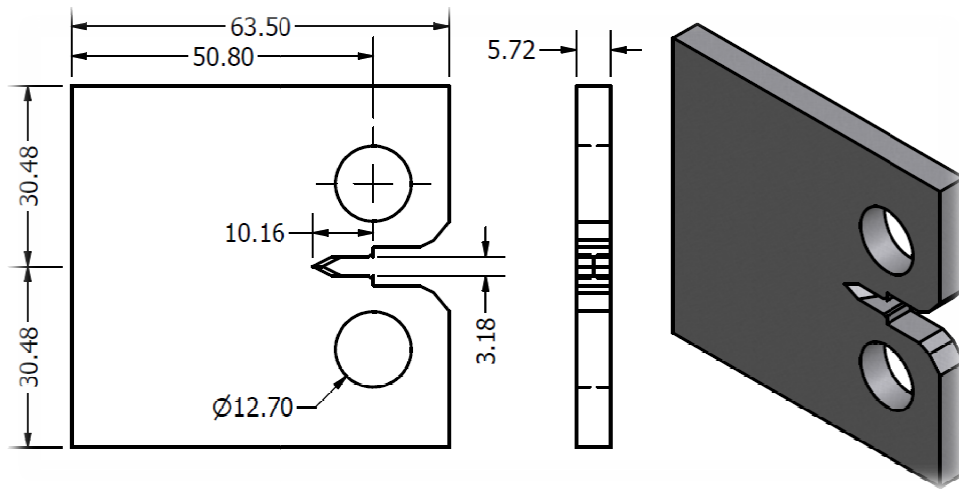


FIGURE 4: Engineering stress versus engineering strain data from tensile tests for the A36, X42, and X70 materials in the longitudinal and transverse orientations.

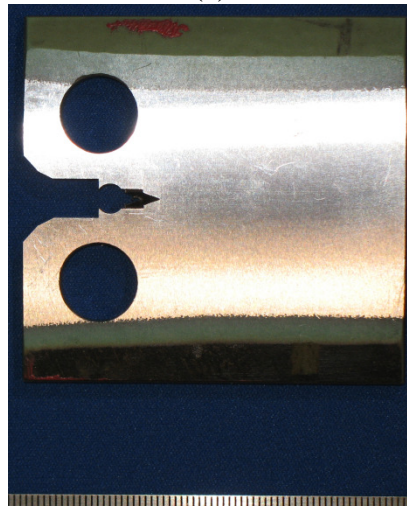
Fatigue Crack Growth Rate (FCGR) Testing

A study of the effects of ethanol based solutions on fatigue crack growth rate (FCGR) in the three materials used in the present study will utilize the compact tension (CT) specimen and a servo-hydraulic load frame equipped with an integrated reaction frame that will allow the specimen to be suspended and fully submerged in a solution during testing. Shown in Figure 4a is a schematic of the CT specimen design to be used in the present study. The specimen design is based on ASTM E-647 for a W of 50.8 mm (2 inch) and a thickness of 5.72 mm (0.225 inch). The specimens were mechanically sectioned from the base material, with the 12.7 mm of material nearest a flame cut edge removed to eliminate the possibility of testing material that have been affected by the flame cutting process. The specimen orientation aligned the notch such that the crack will propagate along the rolling direction of the plate and along the pipe axis. The specimen thickness was selected to be equivalent for the three materials to eliminate specimen geometry aberrations between them. In addition, the thickness was also selected such that a maximum constant thickness could be achieved for all materials in between the far edges of the loading pin holes. Figure 4b shows a photograph of a CT specimen for the X70 material, the specimen does not retain constant thickness outside of the loading pin holes, which is due to the curvature of the pipe. The specimen curvature outside of the loading pin holes is not thought to pose a concern for the data integrity.

A reaction frame to accommodate the loading of the specimen while suspended in a fluid bath is currently being designed and fabricated for use at NIST in Boulder, CO. Initial specimens have been sectioned and machined as shown in Figure 4b, and a test matrix is currently being evaluated to determine the appropriate test solutions for the current research program. The mechanical testing lab is being equipped with an *in situ* ventilation system to vent any ethanol/fuel vapor safely out of the lab per safety requirements.



(a)



(b)

Figure 4: (a) Schematic of specimen geometry for the compact tension, C(T), specimen used for fatigue crack growth rate (FCGR) analysis in the present program, units in mm. (b) Photograph showing a compact tension, C(T), specimen for the X70 material used in the present study. The selected thickness allows for a maximum constant thickness to be achieved within the boundaries of the two pin loading holes. The scale increments are mm.

Conference Paper Submission

The paper “Microbiological and Electrochemical Evaluation of Corrosion and Microbiologically Influenced Corrosion of Steel in Ethanol Fuel Environments” was written for, submitted to, and approved for CORROSION 2010 Conference and Expo (March 14 – 18, 2010, San Antonio, TX, U.S.A.). The paper will be presented during the Biofuel Corrosion Issues Symposium March 16, 2010: 2:00 PM-6:00 pm). A copy of the paper will be uploaded as a supporting document with this report.

Results and Conclusions:

- Corrosion problems have been reported at fueling terminals exposed to water/ethanol mixtures
- Reports of a vinegar smell has been reported in ethanol containment tanks
- Some type of microbes are able to convert ethanol to acetic acid
- Light microscopy indicates the presence of microbes in tank bottoms samples from ethanol spillage tanks
- Putative sulfate-reducing, spore-forming microbes have been isolated from soils exposed to E10, E85, and E100
- Two phase mixtures of E10 and water have produced extensive corrosion and microbiological growth on coupons submerged in the aqueous layer under the organic layer.
- Mechanical properties have been characterized for sample ASTM A36, API X42, and API X70 steel by tensile testing in accordance with ASTM E-8 in the longitudinal and transverse directions of the pipe
- A reaction frame to accommodate the loading of the specimen while suspended in a fluid bath for FCGR testing is currently being designed and fabricated for use at NIST in Boulder, CO.
- Initial Compact tension (CT) specimens have been sectioned and machined for FCGR testing
- Test matrices are currently being evaluated to determine the appropriate test solutions for the current research program.
- The mechanical testing lab at NIST in Boulder, CO is being equipped with an *in situ* ventilation system to vent any ethanol/fuel vapor safely out of the lab per safety requirements.

Issues, Problems or Challenges:

Plans for Future Activity:

- Conduct further thin-film and growth experiments to determine the potential for microbes to survive in high ethanol environments and the potential for spore-forming microbes to effect corrosion
- Continue to analyze 16S rRNA gene data as well as conduct cultivation experiments to support field assessment
- Cultivated microbes on bend specimen prior to cyclic loading
- Calibrate the MSBF and bath assembly
- Begin testing with the MSBF
- Develop and refine a MIC/ethanol review paper
- Characterize the role of variables such as salts, gasoline, denaturants and microbes on the corrosion behavior of steel using electrochemical impedance spectroscopy (EIS), to select environments for mechanical testing
- Perform in-situ electrochemical analysis on the cyclically loaded steel specimens in ethanol-gasoline mixtures both without and with microbes